

# Thermodynamic Measurements on the Binary System Bis{[2,2-di(*n*-hexyloxy carbonyl)ethenyl]phenyl} Biphenyl-4,4'-dicarboxylate and 4-*n*-Octyloxyphenyl 4-*n*-Pentyloxybenzoate at Elevated Pressures

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Thermodynamic measurements have been carried out on the binary system of a swallow-tailed liquid crystal A = bis{[2,2-di(*n*-hexyloxy carbonyl)ethenyl]phenyl} biphenyl-4,4'-dicarboxylate (4DS6) and B = 4-*n*-octyloxyphenyl 4-*n*-pentyloxybenzoate (5O/O8). A filled smectic A phase is induced in the concentration range  $0.11 < x_A < 0.75$ . The maximum of the SmA-N transition temperature (365 K) is observed for  $x_A = 0.33$ . Dilatometric measurements show that the packing density in the filled phases is increased. High-pressure DTA is employed in order to investigate the coexistence range of the liquid crystalline phases and the slopes of the transition lines. The slopes of the melting curves for the mixtures are significantly smaller than those for the pure components. The slopes for the smectic - nematic - isotropic transitions are considerably larger. The coexistence range for the (smectic + nematic) phases does not seem to be pressure-limited, rather it increases with pressure.

**Key words:** Phase Transitions; DTA; High Pressure; Swallow-tailed Liquid Crystals.

## 1. Introduction

The anisometric shape of the molecules is an important precondition for forming mesophases which also dominates the phase structures. Nematic and smectic phases result from calamitic molecules, and columnar phases are formed by discotic molecules. A bent molecular shape leads to a new type of phases, designated as B<sub>n</sub> phases, which are not compatible with conventional smectic phases [1, 2].

Most of the liquid crystals used for practical application are derived from calamitic mesogens. The design of those and the molecular shape can be modified by the introduction of additional long-chain as well as bulky groups in terminal or lateral positions, thus changing significantly the physical properties [3]. Laterally aryl-branched compounds are wedge-shaped mesogens revealing high clearing temperatures and packing densities [4]. Recently, some of them were subjected to high-pressure studies in order to investigate the influence of the density [5, 6].

The shape of the molecules is clearly of influence on the miscibility behaviour resulting in interesting effects [7]. For example, the anisotropic packing of laterally arylsubstituted mesogens is also stable in mixtures with an unexpectedly high share of small, non-mesogenic components [8]. In double-swallow tailed compounds both terminal positions of the rod-like mesogenic core are substituted by two long-chain groups and therefore the shape of the molecules is a dump-bell like, which gives rise to the formation of new phases and phase sequences [9 - 11]. In binary mixtures of such double-swallow tailed compounds with rod-like nematogenic components a smectic A phase is induced, which is not observed in the pure compounds. It is assumed that the short rods fill the gaps caused by the bulky parts of the terminally branched mesogens, leading to an induced "filled smectic A phase", especially for steric reasons [12, 13]. Dielectric measurements were performed to study the mobility of a polar two-ring compound in a filled phase [14]. Furthermore, such systems were

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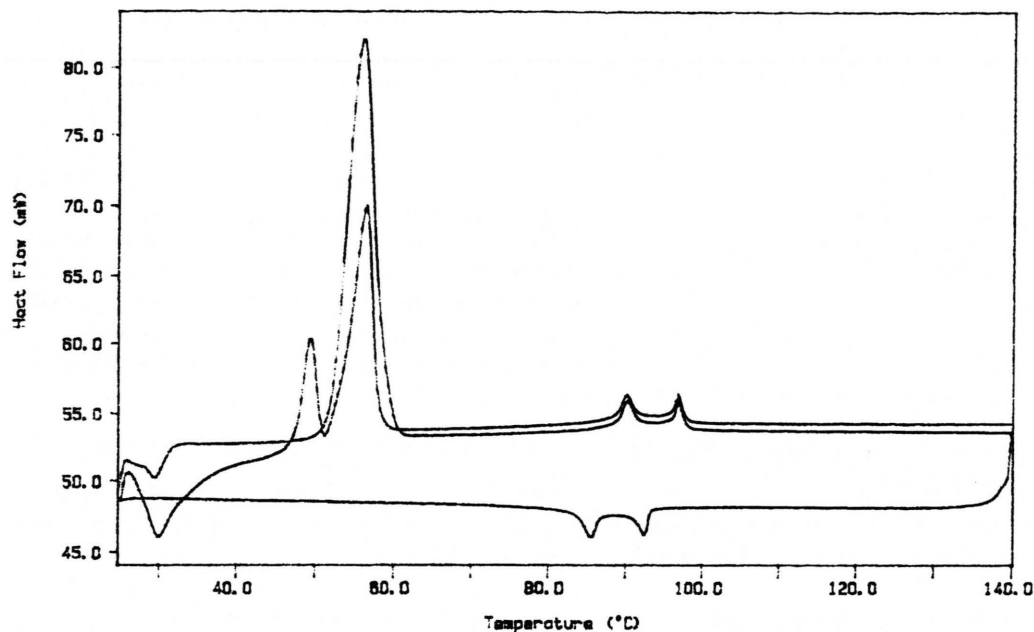
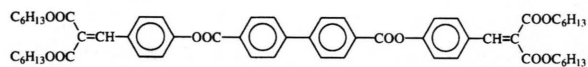


Fig. 1. Selected DSC traces for the mixture  $x_A = 0.16$ .

dilatometrically studied, showing that the packing density in the filled phases is increased [15].

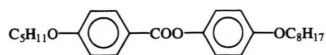
In the present work we choose the following system for a thermodynamic investigation:

A = Bis{[2,2-di(*n*-hexyloxycarbonyl)ethenyl]-phenyl} biphenyl-4,4'-dicarboxylate (4DS6)



Cr 354 K ( $S_C$  341 K) N 398 K Is [16],

B = 4-*n*-Octyloxyphenyl 4-*n*-pentyloxybenzoate (5O/O8)



Cr 323 K N 356 K Is [15].

The phase behaviour of 4DS6 was detected by polarizing microscopy and X-ray studies. It is remarkable that single double-swallow tailed compounds are able to form smectic C phases, but never a smectic A phase was found.

DSC and density measurements are carried out in order to establish the phase diagram. The pressure dependences of selected phase transitions are determined with DTA and compared with those reported for other liquid crystals.

## 2. Experimental

DSC measurements have been carried out with commercially available Perkin-Elmer DSC 7 devices in Halle. The densities were determined with a vibrating tube densimeter Anton Paar DMA 60 [15]. DTA measurements were performed with two high-pressure apparatus which have been constructed for studies at higher and lower temperatures [17,18]. Transition temperatures are derived from DTA thermograms usually obtained on heating. The double-swallow tailed compound 4DS6 was prepared according to [16].

## 3. Results and Discussion

### 3.1. Measurements at Atmospheric Pressure

Figure 1 shows DSC curves for the mixture  $x_A = 0.16$ . The large peak of melting and two smaller peaks are clearly discernable. Accordingly the phase diagram is presented in Fig. 2 (after [15]) displaying a "filled SmA phase" in the range  $0.11 < x_A < 0.75$ . The maximum of the SmA-N transition temperature ( $92^\circ\text{C} = 365\text{ K}$ ) is observed for  $x_A = 0.33$ . The clearing temperature (N-Is) has no maximum. On cooling pure 4DS6 a monotropic smectic C phase has been detected. Obviously various metastable phases

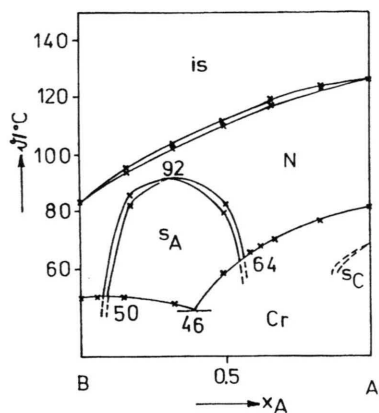


Fig. 2. Phase diagram of the binary system A (4DS6) - B (5O/O8) at atmospheric pressure.

are formed after freezing (also for the mixtures) leading to different melting temperatures and enthalpies on reheating.

The enthalpy changes for 4DS6 are:  $\Delta H_{Cr \rightarrow N} \approx 35$  J/g,  $\Delta H_{N \rightarrow Is} \approx 0.27$  J/g; for 5O/O8:  $\Delta H_{Cr \rightarrow N} \approx 102$  J/g,  $\Delta H_{N \rightarrow Is} \approx 3.4$  J/g. The extremely small clearing enthalpy of 4DS6 renders the calorimetric

measurements (and the high-pressure DTA, see next chapter) of the A-B system rather difficult. DSC results for the mixtures are:  $x_A = 0.16$ :  $\Delta H_{Cr \rightarrow SmA} \approx 60$  J/g,  $\Delta H_{SmA \rightarrow N} \approx 1.76$  J/g,  $\Delta H_{N \rightarrow Is} \approx 1.2$  J/g;  $x_A = 0.33$ :  $\Delta H_{Cr \rightarrow SmA} \approx 37$  J/g,  $\Delta H_{SmA \rightarrow N} \approx 1.45$  J/g,  $\Delta H_{N \rightarrow Is} \approx 1$  J/g;  $x_A = 0.50$ :  $\Delta H_{Cr \rightarrow SmA} \approx 35$  J/g,  $\Delta H_{SmA \rightarrow N} \approx 0.36$  J/g,  $\Delta H_{N \rightarrow Is} \approx 0.4$  J/g.

The molar volume of the induced SmA phase is smaller than that calculated from the additivity rule (see Fig. 3). This corroborates the higher packing density of the filled phases. This is not always so. There are other systems of filled phases, for which the excess volume is positive [15].

### 3.2. DTA Measurements at Elevated Pressures

It was very difficult to follow the SmA - N and N - Is transitions in the high-pressure DTA measurements because of the too small enthalpy change. The clearing temperature of 4DS6 could not be detected. The melting and N  $\rightarrow$  Is transitions of 4DS6, 5O/O8, and the 1:1 mixture are presented in Figure 4. The SmA - N transition of  $x_A = 0.5$  was not visible as a peak, but few degrees below the expected transition a strong

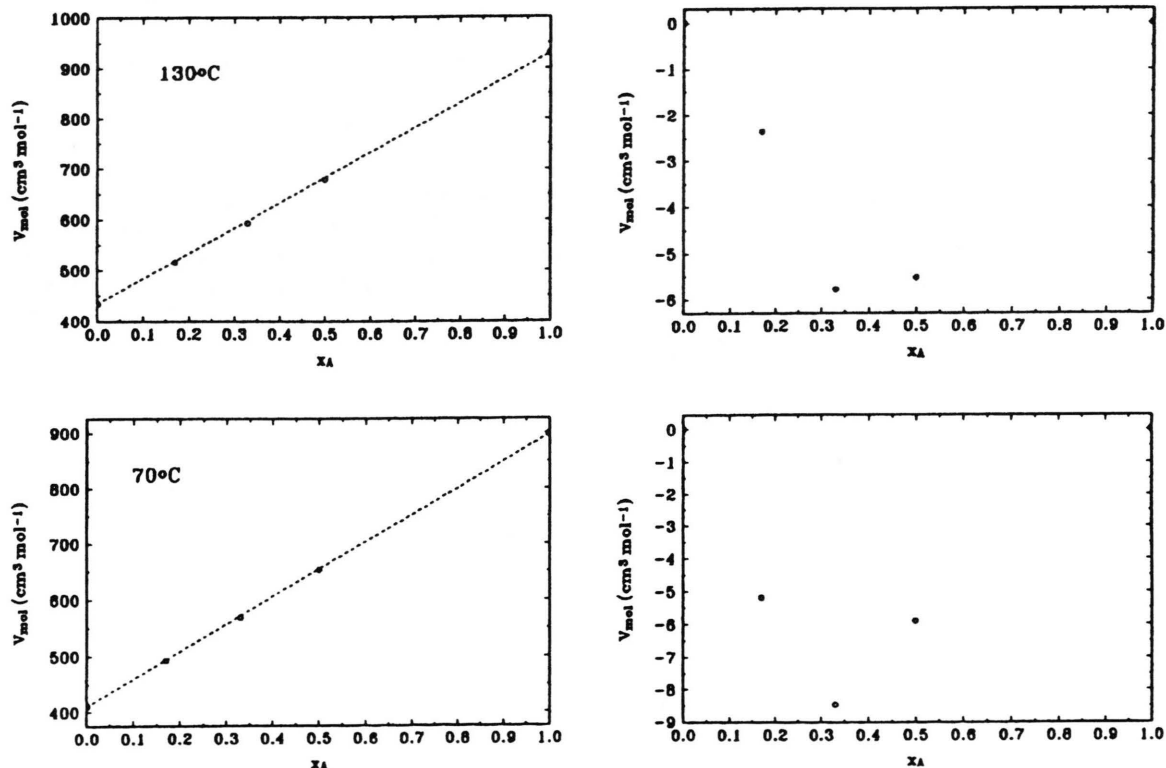


Fig. 3. Molar volumes of the system A - B at atmospheric pressure.

Table 1. Thermodynamic results from the DSC and DTA measurements.

Transition	DSC		DTA		
	$T$ /K	$\Delta H$ /J mol <sup>-1</sup>	$T/K$ (1 atm)	$dT/dp$	$\Delta T/K$ (100 MPa)
4DS6 ( $M = 959.14$ g mol <sup>-1</sup> ):					
Cr → N	356	35	352.1	0.247	18
N → Is	407.5	0.27	399.0		
5O/O8 ( $M = 412.55$ g mol <sup>-1</sup> ):					
Cr → N	323.7	102	320.9	0.245	23
N → Is	360.3	3.4	357.2	0.290	27
$x_A = 0.16$ :					
Cr → SmA	325.3	60	320.8	0.165	19
SmA → N	362	1.76	359.2	0.308	24
N → Is	369	1.2	365.1	0.386	30
$x_A = 0.33$ :					
Cr → SmA	336	37	332	0.192	16
SmA → N	364/368	1.45	364	0.289	25
N → Is	375	1	371	0.359	32
$x_A = 0.50$ :					
Cr → SmA	334	35	330.1	0.174	18
SmA → N	361	0.36	344	0.206	20
N → Is	381	0.4	379	0.283	23

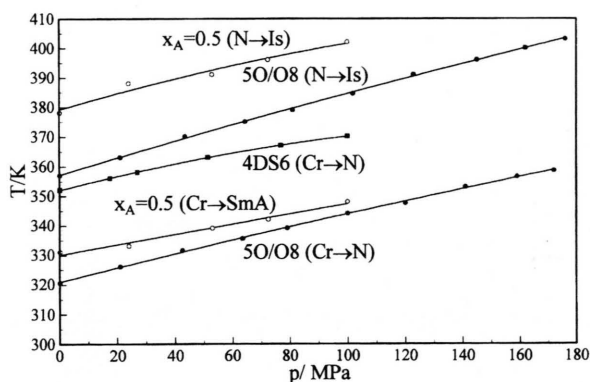
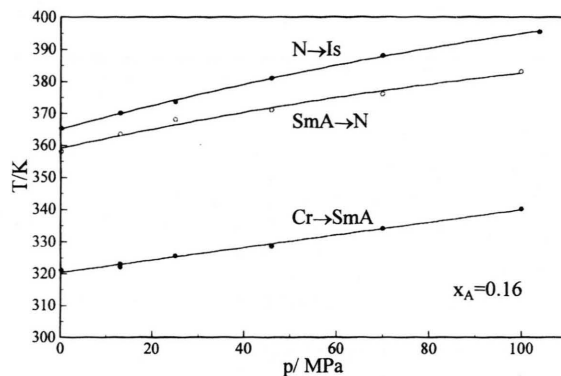


Fig. 4. Phase diagrams of 4DS6, 5O/O8, and the mixture 1:1.

shift of the DTA base line was observed at all pressures (included in Table 1, but not shown in the Figure). Regarding the phase diagram (Fig. 3)  $x_A = 0.5$  meets the steep part of the phase boundary that makes the measurements more difficult. The clearing line of 4DS6 could not be measured. In Fig. 5 the mixture  $x_A = 0.16$  is displayed. The atmospheric transition temperatures and initial slopes  $dT/dp$  are presented in Table 1.

Fig. 5. Phase diagram of the mixture  $x_A = 0.16$ .

The slopes of the melting curves for the pure components ( $\sim 0.25$  K/MPa) are comparable to rod-like nematogens, but somewhat smaller than those of aryl-branched mesogens [5, 6, 19]. The slopes for the mixtures are significantly smaller. However, when the overall compression in the 100 MPa pressure range is considered ( $\Delta T$  (100 MPa) in Table 1) the differences are less pronounced. In general the slope of isochoric lines,  $(dT/dp)_V$ , is considerably larger than the slopes of the phase transition lines,  $(dT/dp)_T$  [5, 6, 20 - 23]. This means the flatter the phase line the more the density increases along that phase line.

The slopes for the smectic - nematic - isotropic transitions are considerably larger. Thus the coexistence range for the (smectic + nematic) phases does not seem to be pressure-limited, rather it increases with pressure. The same behaviour was recently found for some nDBTs [20]. For 4CNOUB [6] the smectic A phase region is pressure-limited resulting in a triple point Cr - SmA - Is. The rod-like liquid crystals 8CB and 8OCB have a pressure-limited SmA region adjacent to the nematic phase [24]. For higher members of the alkylcyanobiphenyls the smectic A phase region is not pressure-limited [25]. For further discussion of density effects the reader is referred to [23, 26].

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